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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF  
JAN MALIK ET AL.  
SERIAL NO. 09/868,871  
FILED: JUNE 5, 2001  
FOR: Stabilizer compositions

Group Art Unit: 1714  
Examiner: Tae H Yoon

Commissioner of Patents and Trademarks  
Washington, D.C. 20231

DECLARATION UNDER RULE 132

I, Andreas Thürmer, a citizen of Germany, residing in D-79576 Weil am Rhein, Bundesland Baden-Württemberg, Germany and hereby declare:

1. That I have have been awarded the degree of "Diplomchemiker" (chemical engineer) in 1988 by "Johann Wolfgang Goethe Universität" Frankfurt am Main and worked for the Max Planck Institut for Polymer Science in Mainz, Germany until 1992.
2. That I have been employed by Sandoz Huningue in March 1992, later Clariant Huningue S.A. as Application Specialist for Additive formulations for Polymers in the Department for Polymer Additives. Since 1999 I have been employed by Ciba Specialty Chemicals Inc., in 1999 as Head of Global Skill centers Molding and Extrusion of the R&T department of the Polymer Additives segment and and presently hold the position of a Global Account Executive in the Polymer Additives Department PA 50.
3. That I have been engaged in screening and development in the field of antioxidants and process stabilizers for polyolefins for Clariant Huningue S.A. since March 1992, and later on for CIBA Specialty Chemivcals Inc. as well.
4. That I am a co-inventor of U.S. Patent Application Serial No. 09/868,871 to Jan Malik et al. and that I am familiar with the subject matter thereof.
5. That the experiments described in the following have been made under my supervision.

Testing Conditions:

The unstabilized polymer powder [polymer = Linear Low Density Polyethylene (LLDPE)] was dry blended with the additives – as given in Table 1. The obtained dry blends were melt homogenized – pre-extruded – at mild conditions in Collin single-screw laboratory extruder (screw compression ratio 1:3; 80 rev/min) at 210°C flat temperature regime. The extruded polymer strand was water chilled and pelletized.

The pellets were then used for multiple extrusion tests that were done at 240°C in Göttfert Extrusimeter (screw compression ratio 1:3; 70 rev/min). The extruded polymer strand was equally water chilled and pelletized. The pellets obtained after pre-extrusion, 1<sup>st</sup>, 3<sup>rd</sup>, and 5<sup>th</sup> extrusion passes were characterized by melt flow index and by color.

#### Measurements:

The Melt Flow Index (MFI) was measured in SWO Melt Fliker HT at 190°C and 2.16 kg load. Color development was characterized by Yellowness Index (YI) measured by Minolta Spectrocolorimeter.

Table 1: Composition of the tested samples

Sample	Composition (ppm)
1 <sup>a)</sup>	1000 CaSt + 500 AO + 200 4,4'PQ + 100 MPQ + 100 P68 + 60 TNPP + 40 ATP
2 <sup>b)</sup>	1000 CaSt + 500 AO + 200 4,4'PQ + 100 MPQ + 100 P68 + 40 TNPP + 40 DTP + 20 ATP
3 <sup>c)</sup>	1000 CaSt + 500 AO + 450 Sandostab P-EPQ + 50 ATP

CaSt is calcium stearate

AO is pentaerythryl-tetrakis-3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate (Irganox 1010; Ciba Specialty Chemicals Inc.)

4,4'PQ is tetrakis(2,4-di-tert-butylphenyl)-4,4'-diphenylene-diphosphonite

MPQ is bis(2,4-di-tert-butylphenyl)-diphenyl-phosphonit

P68 is tris(2,4-di-tert-butylphenyl)-phosphite

TNPP is tris(nonylphenyl)-phosphite

ATP is  $\alpha$ -tocopherol (Ronotec 201; Hoffmann-La Roche)

DTP is di-tridecyl-3,3'-thiodipropionate

- a) Comparison example which corresponds to Example 3 in DE-A-39 03 218.
- b) Comparison example which corresponds to Example 4 in DE-A-39 03 218. TNPP was used instead of trilauryl-phosphite. In polyolefin stabilization it is known that tri-aryl phosphites (as TNPP) are more effective than tri-alkyl-phosphites like trilauryl-phosphite which are normally not used by polyolefin industry.
- c) Example according to the instant invention.

The total concentration of the stabilizers in every sample is the same – 1000 ppm (not including CaSt).

In the comparative samples 1 and 2 the mixture of 4,4'PQ, MPQ and P68 corresponds to the product Sandostab P-EPQ (see page 12 of the instant application).

## Results:

Table 2: Melt Flow Index and Yellowness Index

Sample	MFI; extrusion passes				YI; extrusion passes			
	0	1	3	5	0	1	3	5
1 <sup>a)</sup>	3.57	3.52	3.44	3.03	-1.41	1.04	5.33	7.62
2 <sup>b)</sup>	3.54	3.56	3.41	3.11	-2.53	0.27	3.86	5.96
3 <sup>c)</sup>	3.58	3.57	3.55	3.51	-2.42	0.16	2.74	5.03

Explanation of footnotes a), b) and c) see end of Table 1.

## Discussion of Results

The obtained results show that the instant synergistic composition according to sample 3 clearly outperforms the stabilizer compositions described in the prior art. The stabilizer compositions according to samples 1 and 2 were not able to protect polyethylene from crosslinking as indicated by lower MFI values obtained after 3 and especially 5 extrusion passes. Sample 3 also shows a much better stability with regard to yellowing.

The stabilizing compositions disclosed in Examples 3 and 4 of DE-A-39 03 218 contain, compared to the instant composition, additional compounds like TNPP [tris(nonylphenyl)-phosphite] or DTP [di-tridecyl-3,3'-thiodipropionate]. Surprisingly, the instant stabilizing composition with less compounds has a better effect in the stabilization of polyethylene. The additional compounds TNPP and DTP are not necessary, nevertheless the degree of crosslinking and the extent of yellowing is better than in the Examples of DE-A-39 03 218. This result is a clear technical advantage and could not be expected from the cited prior art.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this **22<sup>nd</sup>** day of February, 2006



Andreas Thürmer